

FILTER FOR MOLTEN METAL FILTRATION AND METHOD FOR PRODUCING SUCH FILTERS

Publication number: EP1421042 (A1)

Publication date: 2004-05-26

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Classification:

- **International:** *B01D39/14; C04B38/00; C04B38/06; B01D39/14; C04B38/00; C04B38/06; (IPC1-7): C04B38/00; B01D39/14; C04B38/06*

- **European:**

Application number: EP20020735244 20020411

Priority number(s): EP20020735244 20020411; WO2002EP04049 20020411; EP20010121044 20010901

Abstract not available for **EP 1421042 (A1)**

Data supplied from the *esp@cenet* database — Worldwide

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 March 2003 (13.03.2003)

PCT

(10) International Publication Number
WO 03/020660 A1

(51) International Patent Classification: C04B 38/00,
38/06, B01D 39/14

(21) International Application Number: PCT/EP02/04049

(22) International Filing Date: 11 April 2002 (11.04.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
01121044.0 1 September 2001 (01.09.2001) EP

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ing Werner, Deichmannhaus am Dorn, 50667 Köln (DE).

(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GH, GI,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: FILTER FOR MOLTEN METAL FILTRATION AND METHOD FOR PRODUCING SUCH FILTERS

(57) Abstract: The present invention relates to a ceramic filter for molten metal filtration that comprises a bonded network of graphi-
tized carbon and a method for producing such filters.

WO 03/020660 A1

**FILTER FOR MOLTEN METAL FILTRATION AND METHOD FOR
PRODUCING SUCH FILTERS**

The present invention relates to a ceramic filter for molten metal filtration that comprises a bonded network of graphitized carbon and a method for producing such filters.

For the processing of molten metals it is desirable to remove exogenous intermetallic inclusions such as from impurities of the raw materials, from slag, dross and oxides which form on the surface of the melt and from small fragments of refractory materials that are used to form the chamber or vessel in which the molten metal melt is formed.

Removal of these inclusions forms a homogenous melt that insures high quality of products especially in the casting of steel, iron and aluminum metals. Currently, ceramic filters are widely used due to their high ability to withstand extreme thermal shock due to their resistance to chemical corrosion and their ability to withstand mechanical stresses.

The production of such ceramic filters generally involves the mixing of ceramic powder with suitable organic binders and water in order to prepare a paste or slurry. The slurry is used to impregnate a polyurethane foam which subsequently is dried and fired at a temperature in the range of from 1000 to 1700 °C. By this treatment the combustible material is burned off during

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sintering to produce a porous body. US-A-2,360,929 and US-A-2,752,258 may serve as examples for the common procedure.

Also, an open pore filter that instead of a random distribution of irregular
5 interconnecting passages consists of a series of parallel ducts passing through
the material as generally being made by hydraulic pressing a damp ceramic
powder and organic binder into a mold containing perpendicular pins. A
perforated structure is thus obtained which can be in the form of a disk or
10 block. The perforated article is then fired at a temperature in the range of from
1000 to 1700 °C depending on the final application to produce a perforated
disc. During firing a ceramic and/or glassy bond is developed.

WO 01/40414 A describes the use of pressurized mould. This patent depends
on regulating the pressure inside the mould to obtain porous structure. Also
15 the porosity in this case is not fully open. The claim of filtration usage is one of
many usage and there is no prove that the filter was ever actually used to
metal filtration. Also only aluminium was mentioned for filtration since such
filter is too weak for steel filtration. The patent describes only a carbon filter
without any ceramic. The process of making the filter is based on regulating
20 the pressure inside the mould. This process is difficult to control.

US-A-4,514,346 uses phenolic resin to react with silicon at high temperature
to form silicon carbide. There is no carbon bonding involved. This patent is for
making porous silicon carbide only. Temperature in excess of 1600 °C is used
25 to obtain silicon carbide. The process is non-aqueous. The porosity obtained
from this process is closed porosity which has no use in filtration requiring
open porosity.

GB-A 970 591 deals with making high density low permeability graphite
30 articles. It uses an organic solvent, namely furfuryl alcohol as solvent and not
water. Binder in the form of pitch is used at 25 % with no ceramic at all. Final

heating is in excess of 2700 °C. The porosity is closed porosity rather than open porosity.

US-A-3,309,433 describes a method for manufacturing high density graphite.

5 It uses hot pressing as a means to obtain high density graphite articles for nuclear applications. It used special material called Dibenzanthrone to bind the graphite. It has no useful application in metal filtration field. It does not use any ceramic in the process. It uses high temperature of up to 2700 °C.

10 EP 0 251 634 B1 describes an appropriate process for making defined porous ceramic bodies having smooth walled cells formed by the pore formers, and pores with round edges, which interconnect the cells.

15 US-A-5,520,823 relates to filters for aluminium only. The bonding is obtained using borosilicate glass. Firing is carried out in air and a considerable amount of graphite would be lost due to the oxidation by air.

20 Filters used for aluminium filtration are usually fired at around 1200 °C while those intended for the use of Iron are fired at temperatures of 1450 °C and for steel at above 1600 °C.

Despite their wide spread use for metal filtration ceramic filters of the above mentioned types have several drawbacks that limit their applicability:

25 1. Ceramic filters, although preheated, tend to be clogged by freezing particles on the first contact with the molten metal. For this purpose usually superheated molten metal that is metal at a temperature of about 100 °C over liquidus temperature is used for casting to prevent clogging of the filters. This practice is extremely wasteful in terms of energy and cost and any improvement
30 that reduces processing temperature of the molten metal is of great benefit. Carbon coatings have been applied in the prior art on the surface of ceramic

filters to reduce the thermal mass of the part that comes into direct contact with the molten metal.

Also an exothermically reacting thermite material applied to a carbon-coated surface of the ceramic filter has been proposed by EP 0 463 234 B1. The latter solution, while reducing the temperature necessary for the flow of the molten metal, adds to the cost of production of the filters and very narrowly limits the applicability as the thermite coating has to be in compliance with the type of molten metal for which it is used.

Anyway, both carbon and thermite coating serve in overcoming the drawback of high thermal mass of the ceramic filter while the challenge of several more disadvantages is not met.

2. Ceramic and glassy type bonds tend to soften and creep at high temperature which very often results in erosion of the filter and subsequent contamination of the melt.

3. Cracking due to thermal shock or chemical (reductive) corrosion by the hot metal melt is a problem often encountered with ceramic and glass bonded filters.

4. The need for extremely high firing temperatures, especially in the case of ceramics intended for steel filtration, is a severe drawback of conventional ceramic filters which is even worse when the need for high cost - ceramic raw material is considered.

5. In addition, the use of zirconia with its relatively strong background radiation is hazardous and should be avoided.

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The object of the present invention is thus to provide an improved filter for metal filtration which overcomes these shortcomings of conventional ceramic or glassy bonded filters.

- 5 In the ceramic filter suitable for molten metal filtration according to the present invention a three dimensional network of graphitizable carbon bonding is used to bind ceramic powder.

- 10 In a first embodiment of the invention relates to a ceramic filter suitable for molten metal filtration comprising a bonded network of graphitized carbon.

- 15 The term „graphitizable“ means that the carbon bonding obtained by pyrolysis of the carbon precursor can be converted into a graphite like bonding on heating to a higher temperature in the absence of air. Graphitizable carbon is distinguished from that of a glassy carbon by the fact that it is impossible to convert glassy carbon to a graphite like bond no matter how high temperature it was heated to.

Carbon bonding of this type exhibits the following advantageous features:

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1. Significantly cheaper to produce.
2. Firing can be carried out at much lower temperature in order to develop the full carbon bonding network from the carbon bond precursor. In general the filters have to be fired at a temperature in the range of from 500 °C to 1000 °C.
- 25 3. Significantly lower superheat is required.
4. Low thermal mass.
5. Better thermal shock resistance.
6. Contamination free.

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The carbon bonded filters according to the present invention exhibit a relatively low thermal mass. A result of this is that there is no need to overheat the metal to be filtered which reduces energy consumption.

- 5 Due to the outstanding mechanical strength of the carbon bonding at high temperature no softening or bending can take place during the process of metal casting. This contributes to an even cleaner metal cast.

Graphitizable carbon bonded filters according to the present invention offer the following advantages compared with glassy carbon bonded filters:

1. High oxidation resistance.
2. Low microporosity.
3. Low specific surface.
4. Structural flexibility.
- 1.5 5. Non-brittle behavior.
6. Economical use.

For optimal performance the graphitized carbon that constitutes the bonded network according to the present invention should be present in an amount up to 15 (25) % by weight of the filter, preferably up to 10 (20) % by weight, even more preferred in an amount of at least 2 (5) % by weight up to 5 (15) % by weight.

In one embodiment of the present invention the carbon bonded ceramic filters are produced in a first process comprising the steps:

- a) Impregnating a foam made of thermoplastic material with a slurry containing a graphitizable carbon bonding precursor, ceramic powder, and optionally other additives,
- b) drying, optionally followed by one or two coatings of the same slurry in order to increase the mass, followed by final drying,

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c) firing the impregnated foam in non-oxidizing and/or reducing atmosphere at a temperature in the range of from 500 to 1000 °C, in particular from 600 °C to 700 °C,

whereby the carbon bonding precursor is converted at least partially or fully to a bonded network of graphitized carbon.

In this process the thermoplastic material used for the foam to be impregnated with the slurry preferably contains or consists of polyurethane.

It is advantageous to mix the carbon bonding precursor prior to impregnating the foam with ceramic powder, water, organic binder, and additives to control the rheology, which in one embodiment of the invention may be present in an amount of up to 2 parts by weight, preferably in a range of from 0.1 to 2 parts by weight.

In another embodiment of the present invention a second type of carbon bonded ceramic filter is produced by a process comprising the steps

a) pressing a semi-damp mixture comprising ceramic powder and a graphitizable bonding precursor, and optionally other additives in a hydraulic press,

b) pressing to obtain a perforated article in the shape of a disk or a block,

c) firing the perforated article in non-oxidizing and/or reducing atmosphere at a temperature in the range of from 500 °C to 1000 °C, in particular from 600 °C to 700 °C,

whereby the carbon bonding precursor is converted partially or fully to a bonded network of graphitized carbon.

The source of the carbon bond, that is the carbon bond precursor is preferably high melting pitch (HMP) because it offers optimal properties with respect to workability, cost and product quality. However, it must be noted that other carbon bond precursors can also be used to produce carbon bonded materials, such as synthetic or natural resins and sinterable carbon as long as it is

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graphitizable and converted to a bonded network of graphitized carbon upon firing according to the present invention. Thus, synthetic resin binders that form a glassy carbon which cannot be converted to graphite may not be considered as carbon bond precursors as the product suffers from low oxidation resistance, low mechanical strength, high brittleness and lower heat resistance.

Also, for economical as well as ecological reasons the carbon bond precursor should be compatible with water. However, organic-solvent based carbon bonding precursors may be used as well.

In further embodiments these processes use a slurry (for the production of a carbon bonded ceramic filter of the first type) or a semi-damp mixture (for the production of the carbon bonded ceramic filter of the second type) that comprises:

a graphitizable carbon bonding precursor in the range of from 2 (5) to 15 (25) parts by weight,

ceramic powder in the range of from 0 (20) to 95 (80) parts by weight,

anti-oxidation material in the range of from 0 to 80 parts by weight,

graphite in the range of from 0 to 90 parts by weight,

organic binder in the range of from 0 to 10, in particular 0.2 to 2 parts by weight and,

dispersion agent in the range of from 0 to 4, in particular 0.1 to 2 parts by weight.

Water is added in a quantity as required. For the purpose of slurry-preparation, 20 to 70 part by weight are necessary depending on the nature of the ceramic filler materials. For the semi-damp mixture used for pressing, water is necessary in an amount of from 2 to 10 parts by weight, depending of the nature of the ceramic filler materials.

The ceramic powder may comprise zirconia, silica, alumina, brown fused alumina, magnesia, any type of clay, talcum, mica, silicon carbide, silicon nitride and the like or any mixture thereof. Graphite may also be used as a substitute for ceramic powder.

5 Preferred anti-oxidation materials according to the present invention are metallic powder such as steel, iron, bronze, silicon, magnesium, aluminum, boron, zirconium boride, calcium boride, titanium boride and the like, and/or glass frits containing 20 to 30 weight percent of boric oxide.

10 Organic binders that are preferred according to the present invention are green binders such as polyvinyl alcohol (PVA), starch, gum arabic, sugar or the like or any combination thereof. These binders may be added to improve the mechanical properties of the fillers during handling prior to firing. Starch and
15 gum arabic may also be used as thickening agent.

Preferred dispersion agents according to the present invention are Despex®, ligninsulphonate or the like, or any combination thereof which help to reduce the water level in the slurry and improve the rheology.

20 In a further embodiment of the present invention the slurry or semi-damp mixture may comprise a plasticizer such as polyethylene glycol (preferred molecular weight: 500 to 10000) in the range of from 0 to 2 parts by weight, preferably 0,5 to 1 part by weight and/or

25 an anti-foam agent such as silicon anti-foam in the range of from 0 to 1 part by weight, preferably 0,1 to 0,5 parts by weight.

The invention is further illustrated by the following examples:

Examples:

As graphitizable high melting pitch (HMP) a coal-tar pitch was used having a glass transition temperature of 210 °C, a coking value of 85 %, an ash value of 0,5 % and which was available as a fine powder.

In all examples the resultant mixture was fired in inert atmosphere at a temperature in the range of from 600 °C to 900 °C for 20 to 120 min at a heating rate in the range of from 1 °C/min to 10 °C/min.

A: Filters according to the first type:

A polyurethane foam was cut to the required size and impregnated with a slurry containing all or some of the following, a high melting pitch powder, ceramic powder, anti-oxidant material, organic binder, dispersion agent, anti-foam, etc., as mentioned in Table 1. The filter was either impregnated manually or by a machine containing rollers used for this purpose. After impregnation the filter was dried using hot air and/or a microwave drier. The coating was applied by a spraying air gun. The filter was dried once more and transferred to a firing furnace with reducing or non-oxidizing atmosphere. The furnace was heated at a rate from 1 °C/min to 10 °C/min depending on the composition of the slurry, size of the filter, size of the furnace etc.

Table 1:

Ingre-dients [parts by weight]	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7	Exp. 8	Exp. 9
Zirconia powder	800	600							
Graphite powder		200			250			700	350
Graphite powder			760						
Alumina powder				750	500		700		350
Silicon carbide powder						750			
HMP	200	220	240	220	250	220	40	70	60
Water	320	400	600	370	450	450	210	450	380
Silicon powder					40				
Borate frit powder					30				
Green binder	10								
Thickening agent	3	5	9	5	5	6	2	3	3
Wetting agent			1	1			1	1	1
Dispersion agent	12	15	20	15	15	15	60	100	80
Plasticizer	5	5	5	5	5	5			
Anti-foam agent	1	1	1	1	1	1	1	1	1

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These filters have a modulus of rupture in the range of 0.6 to 1.2 Mpa depending on composition, weight etc. The heavier the filter the higher is the strength. These filters are significantly lighter than those made from ceramic or glass bonded material. They are also significantly cheaper. During field trials it was found that no superheat is required when using these filters since extra heat was generated upon contact of molten metal with the filter (exothermic reaction).

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Also heating these filters to a temperature above 1500 °C results in forming a graphite like bonding. Although such treatment would improve the overall properties of the filter, it is not required for the purpose of molten metal filtration.

15

B: Filters according to the second type:

A mixture was prepared in a Hobart or Elrich mixer, the mixture comprising
5 ceramic powder, high melting pitch, organic binder, plasticizer and water. The
aim of the mixing process was to make a semi-damp and homogenous
mixture. The mixture was aged for 24 hours prior to pressing. A
predetermined weight of the mixture was placed in a steel mold which
10 contained vertical pins. Pressing the mix produced a perforated article. This
perforated article was then removed from the mold, dried and fired in a non-
oxidizing or reducing atmosphere at a temperature of 700 °C for 1 h with a
heating rate of 2 °C/min.

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Table 2:

	1	2	3	4	5	6	7	8	9	10	11	12
Zirconia powder	850				660							
Organic Binder											4	6
HMP		150	200	200	200	200	100	100	150	200	4	3
Cal. Alumina			300	800			250	200	200	200	20	18
BFA	500					450	400	450	400		37	
Graphite				750	200	200	200	100	100		25	23
Silicon								40	40	40	4	4
Borate frit powder							20	20	20		2	4
Feldspar							40	40	40	20		
PVA	20	20	20	25	20	20	20	20	20	2	4	4
PEG (4000)	8	8	8	8	8	8	8	8	8	8	1	0
Water	40	40	40	55	80	40	40	40	40	40	4	4

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The graphitizable carbon bonded perforated filter was used in a field trial to filter molten steel. It was found that the filter did not require molten metal superheat since it generated heat on contact of molten metal with the filter which was enough to keep the molten steel flow during filtration. This was due to the exothermic reaction of the filter surface and the molten steel. Also, the filter did not suffer from thermal shock or distortion during the test. These filters were considerably lighter than those of ceramic or glass bonded material. Ceramic or glass bonded filters require superheat between 80 to 150 °C. This large superheat renders the use of ceramic or glass bonded filters undesirable for steel filtration despite their low cost compared to open pore filters. These advantages will open the door for economic and efficient filtration of casting steel.

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Claims:

1. A ceramic filter suitable for molten metal filtration comprising a bonded
5 network of graphitized carbon.
2. The filter of claim 1 wherein the graphitized carbon constitutes up to 15 %
by weight, in particular up to 10 % by weight.
- 10 3. A method to produce ceramic filters according to claim 1 or 2, comprising
the steps
- a) impregnating a foam made of thermoplastic material with a slurry
containing a graphitizable carbon bonding precursor, ceramic powder, and
optionally other additives,
- 15 b) drying, optionally followed by one or two coatings of the same slurry in
order to increase the mass, followed by final drying,
- c) firing the impregnated foam in non-oxidizing and/or reducing atmosphere at
a temperature in the range of from 500 to 1000 °C, in particular from 600 °C
to 700 °C,
- 20 whereby the carbon bonding precursor is converted at least partially or fully to
a bonded network of graphitized carbon.
4. The method of claim 3 utilizing a thermoplastic foam that contains
polyurethane.
- 25 5. The method of claims 3 or 4 wherein the carbon bonded precursor is mixed
with ceramic powder, water, organic binder, and additives to control the
reology, prior to impregnating the foam.
- 30 6. A method to produce the ceramic filters according to claims 1 or 2,
comprising the steps

- 15 -

a) pressing a semi-damp mixture comprising ceramic powder and a graphitizable bonding precursor, and optionally other additives in a hydraulic press,

b) pressing to obtain a perforated article in the shape of a disk or a block,

5 c) firing the perforated article in non-oxidizing and/or reducing atmosphere at a temperature in the range of from 500 °C to 1000 °C, in particular from 600 °C to 700 °C,

whereby the carbon bonding precursor is converted partially or fully to a bonded network of graphitized carbon.

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7. The method of any one of claims 3 to 7 wherein high melting pitch (HMP) is used as the graphitizable carbon bonding precursor.

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8. The method of any one of claims 3 to 8 wherein a slurry or semi-damp mixture is used comprising:

graphitizable carbon bonding precursor in the range of from 2 to 15 parts by weight,

ceramic powder in the range of from 0 to 95 parts by weight,

anti-oxidation material in the range of from 0 to 80 parts by weight,

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graphite in the range of from 0 to 90 parts by weight,

organic binder in the range of from 0 to 10, in particular 0.2 to 2 parts by weight and,

dispersion agent in the range of from 0 to 4, in particular 0.1 to 2 parts by weight.

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9. The method of claim 8 wherein zirconia, silica, alumina, brown fused alumina, magnesia, any type of clay, talcum, mica, silicon carbide, silicon nitride and the like or a mixture thereof, or graphite, is used as the ceramic powder.

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10. The method of claim 8 or 9 wherein metallic powders such as steel, iron, bronze, silicon, magnesium, aluminium, boron, zirconium boride, calcium

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boride, titanium boride and the like, and/or glass frits containing 20 to 30 weight percent of boric oxide are used as the anti-oxidation material.

11. The method of any one of claims 8 to 10 wherein a green binder such as PVA, starch, gums, sugar or the like or a combination thereof is used as the organic binder.

12. The method of any one of claims 8 to 11 wherein lignisulphonate is used as the dispersion agent.

13. The method of any one of claims 8 to 12 wherein a slurry or semi-damp mixture is used that further comprises:

a plasticizer such as polyethylene glycol (molecular weight: 500 to 10000) in the range of from 0 to 2 parts by weight,

an anti-foam agent such as silicon anti-foam in the range of from 0 to 1 part by weight.

AMENDED CLAIMS

[received by the International Bureau on 16 September 2002 (16.09.02);
original claim 3-13 amended; new claims 14-17 added; remaining claims unchanged]

5.

1. A ceramic filter suitable for molten metal filtration comprising a bonded network of graphitized carbon.

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2. The filter of claim 1 wherein the graphitized carbon constitutes up to 15 % by weight, in particular up to 10 % by weight.

3. A filter suitable for molten metal filtration comprising a bonded network of graphitized carbon.

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4. A method to produce ceramic filters according to **claims 1 or 2**, comprising the steps

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a) impregnating a foam made of thermoplastic material with a slurry containing a graphitizable carbon bonding precursor, ceramic powder, and optionally other additives,

b) drying, optionally followed by one or two coatings of the same slurry in order to increase the mass, followed by final drying,

c) firing the impregnated foam in non-oxidizing and/or reducing atmosphere at a temperature in the range of from 500 to 1000 °C, in particular from 600 °C to 700 °C,

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whereby the carbon bonding precursor is converted at least partially or fully to a bonded network of graphitized carbon.

5. A method to produce filters according to claim 3, comprising the steps

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a) impregnating a foam made of thermoplastic material with a slurry containing a graphitizable carbon bonding precursor, and optionally other additives,

b) drying, optionally followed by one or two coatings of the same slurry in order to increase the mass, followed by final drying,
c) firing the impregnated foam in non-oxidizing and/or reducing atmosphere at a temperature in the range of from 500 to 1000 °C, in particular from 600 °C to 700 °C,
whereby the carbon bonding precursor is converted at least partially or fully to a bonded network of graphitized carbon.

6. The method of claim 4 or 5 utilizing a thermoplastic foam that contains polyurethane.

7. The method of claim 4 wherein the carbon bonded precursor is mixed with ceramic powder, water, organic binder, and additives to control the reology, prior to impregnating the foam.

8. The method of claim 5, wherein the carbon bonded precursor is mixed with water, organic binder, and additives to control the reology, prior to impregnating the foam.

9. A method to produce the ceramic filters according to claims 1 or 2, comprising the steps

a) pressing a semi-damp mixture comprising ceramic powder and a graphitizable bonding precursor, and optionally other additives in a hydraulic press,

b) pressing to obtain a perforated article in the shape of a disk or a block,

c) firing the perforated article in non-oxidizing and/or reducing atmosphere at a temperature in the range of from 500 °C to 1000 °C, in particular from 600 °C to 700 °C,

whereby the carbon bonding precursor is converted partially or fully to a bonded network of graphitized carbon.

10. A method to produce the filters according to claim 3, comprising the steps

a) pressing a semi-damp mixture comprising ceramic powder and a graphitizable bonding precursor, and optionally other additives in a

hydraulic press,

b) pressing to obtain a perforated article in the shape of a disk or a block,

c) firing the perforated article in non-oxidizing and/or reducing atmosphere at a temperature in the range of from 500 °C to 1000 °C,

in particular from 600 °C to 700 °C,

whereby the carbon bonding precursor is converted partially or fully to a bonded network of graphitized carbon.

11. The method of any one of claims 4 to 10 wherein high melting pitch (HMP) is used as the graphitizable carbon bonding precursor.

12. The method of anyone of claims 4 to 11 wherein a slurry or semi-damp mixture is used comprising:

graphitizable carbon bonding precursor in the range of from 2 to 15 parts by weight,

ceramic powder in the range of from 0 to 95 parts by weight,

anti-oxidation material in the range of from 0 to 80 parts by weight,

graphite in the range of from 0 to 90 parts by weight,

organic binder in the range of from 0 to 10, in particular 0.2 to 2 parts by weight and,

dispersion agent in the range of from 0 to 4, in particular 0.1 to 2 parts by weight.

13. The method of claim 12 wherein zirconia, silica, alumina, brown fused alumina, magnesia, any type of clay, talcum, mica, silicon carbide, silicon nitride and the like or a mixture thereof, or graphite, is used as the ceramic powder.

14. The method of claim **12** or **13** wherein metallic powders such as steel, iron, bronze, silicon, magnesium, aluminium, boron, zirconium boride, calcium boride, titanium boride and the like, and/or glass frits containing 20 to 30 weight percent of boric oxide are used as the anti-oxidation material.

15. The method of any one of claims **11** to **14** wherein a green binder such as PVA, starch, gums, sugar or the like or a combination thereof is used as the organic binder.

16. The method of any one of claims **11** to **15** wherein lignisulphonate is used as the dispersion agent.

17. The method of any one of claims **11** to **16** wherein a slurry or semi-damp mixture is used that further comprises:
a plasticizer such as polyethylene glycol (molecular weight: 500 to 10000) in the range of from 0 to 2 parts by weight,
an anti-foam agent such as silicon anti-foam in the range of from 0 to 1 part by weight.

INTERNATIONAL SEARCH REPORT

 International Application No.
 PCT/EP 02/04049

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C04B38/00 C04B38/06 B01D39/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C04B B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 520 823 A (STOETZEL REINHARD ET AL) 28 May 1996 (1996-05-28)	1-5
Y	column 3, line 7 - column 4, line 67	7
X	WO 01 40414 A (TOUCHSTONE RES LAB LTD) 7 June 2001 (2001-06-07)	1
	page 12, line 12 - page 12, line 21 page 14, line 10 - page 16, line 24	
A	US 4 514 346 A (LUHLEICH HARTMUT ET AL) 30 April 1985 (1985-04-30)	1-13
	column 7, line 17 - column 7, line 55	
Y	GB 970 591 A (ATOMIC ENERGY AUTHORITY UK) 23 September 1964 (1964-09-23)	7
	page 3, line 18 - page 3, line 76	
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

8 July 2002

Date of mailing of the international search report

16/07/2002

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INTERNATIONAL SEARCH REPORT

International Application No.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 309 433 A (FRED ROBERTS) 14 March 1967 (1967-03-14) the whole document	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 02/04049

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5520823	A	28-05-1996	AT 135251 T	15-03-1996
			AU 658760 B2	27-04-1995
			AU 4270393 A	04-01-1994
			BR 9306497 A	15-09-1998
			CA 2136335 A1	23-12-1993
			DE 69301825 D1	18-04-1996
			DE 69301825 T2	01-08-1996
			DK 649334 T3	22-07-1996
			EP 0649334 A1	26-04-1995
			ES 2084500 T3	01-05-1996
			WO 9325296 A1	23-12-1993
			JP 7507489 T	24-08-1995
			JP 3247952 B2	21-01-2002
			KR 254287 B1	01-05-2000
			MX 9303306 A1	31-01-1994
			ZA 9303680 A	21-12-1993
WO 0140414	A	07-06-2001	AU 1809601 A	12-06-2001
			WO 0140414 A1	07-06-2001
US 4514346	A	30-04-1985	DE 3005587 A1	20-08-1981
			AT 8774 T	15-08-1984
			CA 1157242 A1	22-11-1983
			EP 0034328 A1	26-08-1981
			JP 1376188 C	22-04-1987
			JP 56129665 A	09-10-1981
			JP 61041867 B	18-09-1986
GB 970591	A	23-09-1964	CH 423731 A	15-11-1966
			NO 115020 B	01-07-1968
US 3309433	A	14-03-1967	DE 1226924 B	13-10-1966
			GB 1053645 A	